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CHARACTERIZATION OF IR WINDOWS

THIRD QUARTERLY TECHNICAL REPORT

by

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Arthur D. Little, Inc.

THIRD QUARTERLY TECHNICAL REPORT

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I. INTRODUCTION AND SUMMARY

High resistivity GaAs has usually been observed to have an optical absorptivity within the range 0.01 to 0.025 cm^{-1} at 10.6μm. This range does not appear to be affected by any of the intuitively important materials parameters--growth procedure, charge compensation element, crystallographic orientation, chemical purity or structural perfection. This suggests that:

a. The intrinsic absorptivity of GaAs at room temperature and 10.6μm radiation is of the order of $10^{-2}cm^{-1}$, or

b. There is some type of defect or structural disorder common to all charge compensated GaAs which is insensitive to variations in process parameters and which prevents the attainment of lower absorptivities.

A detailed characterization study is in progress at Arthur D. Little, Inc., that is expected to resolve this issue, utilizing experimental methods that permit the detection of structural and compositional variations within a size range of 10^{-7} to 10^{-2} cm. Procedures have emphasized direct observation of structure by various methods, including selected combinations of optical and infrared microscopy, reflection and transmission X-ray topography and transmission electron microscopy. Our ultimate objective is to eliminate or minimize defects affecting the optical absorptivity of GaAs by means of appropriate modifications to crystal growth procedures.

Evaluation samples have been supplied by Bell & Howell who, under a concurrent ONR-sponsored program, is striving to prepare high quality low absorptivity GaAs boules with an eventual goal of achieving scale-up to 3 to 12 inches in diameter. They are attempting to minimize absorption through selected variations in growth parameters, including dopant, concentration, growth rate, seed orientation, etc. Bell & Howell has made absorption coefficient measurements on each boule prepared; the approximately 1-cm thick cross section of each boule that is employed for the absorption measurement has subsequently been supplied to ADL for structural characterization. Altogether, 25 samples representing a variety of growth conditions have been received from Bell & Howell. A summary of

measured parameters for these samples is given in Table I. Spark source mass spectrometer measurements of trace elements being conducted by Bell & Howell are not available at present.

During the first quarter of study,[1] our major effort was directed to developing appropriate procedures for sample handling and processing. A considerable effort was devoted to developing high resolution film processing procedures to be assured that no artifacts were introduced that could be misinterpreted as evidence of structural defects. Similarly, techniques were developed so that defects were not introduced during sample preparation, thereby permitting observation of the as-grown defects. Several GaAs crystals available at ADL were employed for developing appropriate sample handling procedures.

During the second quarter,[2] five samples supplied by Bell & Howell and two additional samples obtained commercially were evaluated by optical microscopy, extended Laue and Berg-Barrett back reflection X-ray topography methods. Also considerable attention was addressed to evaluating (1) various types of X-ray sensitive photographic emulsions to obtain maximum recorded resolution, (2) mechanical and mechanical-chemical polishing of as-cut surfaces to remove saw-cut damage, and (3) the thickness of the surface damaged layer that still remained after various polishing procedures, determined via edge X-ray topography.

During the past quarter, studies ~~have included~~ transmission electron microscopy of several of the initially received samples as well as back reflection X-ray topography of two additional lots of samples received from Bell & Howell. The second lot of sixteen samples, representing six different seed orientations, was found in general to exhibit good crystallographic quality, with very little indication of coring or faceted growth. A final lot of four samples from Bell & Howell represented boules grown from gallium-rich melts. The samples prepared from 70 and 65 percent gallium melts exhibited heavy faceting; the other samples showed good crystallographic quality. Transmission electron microscopy on thin sections from the first lot of five samples has revealed evidence for the

presence of very fine (<100Å) defects having a density of 1 to 5 x 10^{17} cm^{-3}. It is probable that they contain Ga and/or As as the total number of impurity atoms is on the order of $10^{16}cm^{-3}$. Initial results indicate that the defects are rod-like coherent precipitates or some other chemically related defect such as clustering or very slightly extended stacking faults.

Preliminary calculations based on assumed metallic or dielectric properties indicate that the observed optical absorptivities at 10.6μ could be caused by these defects. These calculations will be refined as the characteristics of the defects become better defined. We consider these observations extremely important, since this is the first clear indication that the measured optical absorptivities may be the result of a growth defect rather than intrinsic factors related to the GaAs lattice. Thus, lower absorptivities can perhaps be realized by modified growth conditions.

II. EXPERIMENTAL RESULTS

A. Sample Inventory

Twenty-five (25) samples of GaAs have been subjected to some form of characterization. These samples were prepared by Bell & Howell under a concurrent ONR-sponsored program.[3] Most of the crystals were grown by the Czochralski technique under liquid B_2O_3 encapsulation, utilizing seeds oriented to <111>A and B, <100>, <110>, <311> and <511> directions. Some of the samples were grown from non-stoichiometric melts containing 55 to 70 atomic percent gallium.

Evaluation slices were generally taken from the top and bottom of each ingot. The cut faces of the slices were mechanically lapped with 600 and 1200 grit SiC followed by polishing on silk charged with 0.3μm Al_2O_3 (Linde B). Measured dislocation densities were typically in the range $2 \times 10^3 cm^{-2}$ at the top to $2 \times 10^4 cm^{-2}$ at the bottom. Optical absorptivities at 10.6μm fell within the range 0.010-0.020 cm^{-1}; variations in orientation, surface preparation, trace element chemistry and stoichiometry did not appear to significantly influence the optical absorptivity.

Experiment parameters obtained for the various samples received are summarized in Table I. A more detailed discussion of the crystal growth and property measurements is given by Thompson.[3]

B. X-ray Topography

The second and third lots of samples were screened by back reflection X-ray topography, utilizing CuK_α radiation and a (422) reflection. As a group, the crystals grown under liquid encapsulation appear to have much better crystallographic uniformity than those utilizing a sealed magnetic puller.[1] The gross crystallographic structures of these samples can be summarized as follows:

Uniform	Slight Faceting	Heavy Faceting
6001T and B		
6002T		
6003T	6003B'	
6005T	6005B	
6008T	6008B	
	6018T, T' and B	

Uniform	Slight Faceting	Heavy Faceting
6047T and B		
6051T	6051B	
6052		
6053		
		6055
		6056

It is interesting to note that the top section of an ingot is never less perfect than the bottom portion. As noted previously,[1] there is no correlation between gross structural perfection and optical absorption coefficient. The nine samples having a uniform structure have an average absorption coefficient of 0.0174 cm^{-1}, whereas the equivalent average for the seven slightly faceted samples is 0.0176 cm^{-1}; the overall range in coefficient is 0.010-0.021 cm^{-1}.

Several of the samples (6003B', 6005B and 6018B) exhibited localized areas along their periphery where breakdown to a polycrystalline structure occurred. A typical example of this breakdown is shown in Figure 1a. These regions probably result from a disruption of the liquid encapsulant seal, leading to a localized enrichment in gallium and ultimately to a breakdown of the structure to allow accommodation of the induced lattice strain. All of the samples exhibited surface damage resulting from mechanical polishing. The magnitude of this damage is exhibited in Figure 1b. Two samples having surfaces carefully prepared by Bell & Howell to minimize surface damage were observed to have the same density of surface defects as all the other samples.

C. Transmission Electron Microscopy

As no correlation was obtained between measured values of optical absorptivity at 10.6μ and observed structural features larger than 10^{-4} cm in extent (stress induced by faceted growth, cellular growth, etc.), transmission electron microscopy (TEM) has been employed to search for lattice defects on the 10^{-7} to 10^{-4} cm range. Initial studies have been carried out on samples that had previously thinned down to 1-3μm by ion bombardment in preparation for examination by transmission X-ray topography. Small sections of these samples were further thinned chemically

in $1HF:3HNO_3:4H_2O$ until pinhole breakthrough occurred or in an ion thinner specially designed for preparing TEM samples. Areas surrounding the pinhole were usually thin enough for electron transmission, i.e., less than 1000Å. A summary of samples examined and others scheduled for examination is given in Table II.

As ion thinning was previously noted to produce surface craters,[2] all additional samples for TEM will be mechanically polished down to about 0.002 inches thickness with final thinning conducted in both the ion thinner and chemically. It is hoped thereby to have more uniformly thinned samples than could be obtained from blanks having craters. Chemical thinning will be used to assure that there is no radiation damage caused by the ion bombardment. Chemical methods, however, generally result in the formation of surface artifacts, such as oxides, and are less desirable.

To date, samples have been examined for the most part with a Siemens Model 101 electron microscope operated at 120kv An extremely fine structure has persistently been observed in every sample examined. A typical photograph of this "salt and pepper" structure along with the corresponding diffraction pattern is presented in Figure 2. The diffraction pattern shows rel-rod streaks extending in <110> directions. Many of the rel-rods extend to a point of common intersection, forming a framework lattice structure. This framework is shown more clearly in Figure 3, obtained from a foil closely oriented to (111). Kikuchi lines and bands are also abundantly present in the pattern indicating a fairly thick foil, probably in excess of 500Å. Reflections having non-vanishing structure factors are indexed in the accompanying sketch.

The intersection of <110> rel-rods appears as a discrete spot in the diffraction patterns. The formation of extra spots is generally accounted for by

a. Double diffraction effects;
b. Extended rel-rods from reciprocal lattice points directly above and below the imaged plane;
c. Contrast enhancement due to the overlapping of three rel-rods.

Case (a) is ruled out, since these e.. ra spots have non-rational coordinates. Furthermore, attempts to produce a dark field image of these extra spots has been unsuccessful, probably ruling out Case (b). Therefore, the apparent appearance of spots is probably caused by Case (c).

Streaking such as is observed in the electron diffraction patterns of these samples is generally associated with a localized rearrangement of solute to form small regions (less than 100Å in extent) having a composition different than the parent matrix. These precipitates are usually totally coherent with the matrix. Rel-rods, or streaks, can result from one or more very thin dimensions in the second phase (i.e., a plate or rod morphology), coherency strains, or periodic lattice modulations based on variations in composition or atomic order, i.e., a stacking fault. Observation of the very fine "salt and pepper" structure and streaked electron diffraction patterns in all GaAs samples examined to date strongly suggests the presence of very small, second-phase precipitates. Samples are being prepared in a (110)-foil orientation, which should allow unequivocal interpretation of the observed fine structure.

All samples examined provided an extremely fine microstructure as is shown in Figure 2. In order to produce the highest image resolution, several photographs were taken by the weak beam technique. A representative image and corresponding diffraction pattern are presented in Figure 4. Careful image analysis yields a defect count of $3 \times 10^{17} cm^{-3}$, assuming a 1000Å foil thickness. As there are about 4×10^{22} atoms cm^{-3} in GaAs, the volume fraction of defects is about 10^{-5}. Because the total level of impurities in this GaAs is also not more than 10^{-5}, the defects must be associated with compositional fluctuations involving Ga and/or As.

Very preliminary calculations of optical absorptivity according to the Mie theory of phonon interactions with spherical particles[4] yield absorption coefficient values of approximately 0.2 cm^{-1} for the observed concentration of defects, assuming them to be intermediate electrical conductivity metallic spheres with diameters of 5 to 25Å. Although these calculations will have to be refined as the characteristics of the defects

are better defined, they indicate that the observed optical absorptivities may be due to st uctural defects and are not intrinsic to GaAs.

III. FUTURE WORK

During the final quarter of study, selected samples from those listed in Table I, especially including those with the lowest measured absorptivities, will be prepared in thin sections for transmission X-ray topography. These sections will subsequently be thinned further for examination of selected areas by transmission electron microscopy. TEM studies will be continued, employing other foil orientations to elucidate further the nature of the observed defects reported herein. Depending upon the observed size and shape of the defects, more rigorous computations will be made of the theoretical absorption coefficient for comparison to experiment.

IV. REFERENCES

1. John S. Haggerty and Edward T. Peters, "Characterization of IR Windows," First Quarterly Technical Report, Arthur D. Little, Inc., March 1972, Contract N00014-72-C-0092.
2. John S. Haggerty and Edward T. Peters, "Characterization of IR Windows," Semiannual Technical Report, July 1972.
3. A.G. Thompson, "Development of GaAs Infrared Window Material," Final Technical Report, Bell & Howell, July 1972, Contract N00014-70-C-1032.
4. H.C. Van De Hilst, Light Scattering by Small Particles, J. Wiley & Sons, 1957, p. 271.

TABLE I

SUMMARY OF SAMPLES RECEIVED FROM BELL & HOWELL

Sample No.[a]	Orientation	Growth Speed (cm/hr)	Resistivity ($\times 10^6$, ohm-cm)	Optical Absorption at 10.6μm[b] (cm^{-1})	Remarks
LOT 1					
1852T	<111>A	1.9	35	0.031	(c)
1857T	"	"	25	0.013	(c)
1860T	"	"	90	0.018	(c)
1860B	"	"	90	0.019	(c)
2002-10T	"	"	50	0.016	
LOT 2					
6001T	<111>A	1.9	3.7	0.014	
6001B	"	"	2.2	0.016	
6002T	"	1.3	5.3	0.020	
6003T	"	2.5	11	0.021	
6003B'	"	"	41	0.014	(d)
6005T	<100>	1.9	190	0.021	
6005B	"	"	85	0.017	
6008T	<111>B	1.3	64	0.021	
6008B	"	"	25	0.017	
5018T	~<331>	"	18	0.020	
6018B	"	"	65	0.020	
6018B'	"	"	65	0.018	(e)
6047T	<551>	"	82	0.015	
6047B	"	"	66	0.010	
6051T	<110>	"	48	0.019	
6051B	"	"	46	0.017	
LOT 3 (Grown from Ga-rich melts)					
6052	<111>A	0.6	6.9	0.019	55% Ga melt
6053	"	0.6	8.2	0.015	60% Ga melt
6055	"	0.6	2.2	0.010	65% Ga melt
6056	"	0.3	$<10^3$ ohm-cm	---	70% Ga melt

(a) T = top of ingot, B = bottom of ingot (more than 1/2 of melt pulled)

(b) All samples were 0.5-1 cm thick; faces were mechanically polished with 0.3μm Al_2O_3 (Linde B).

(c) Utilized sealed magnetic puller; all other samples grown under liquid B_2O_3 encapsulation.

(d) With normal surface treatment, $\alpha = 0.014\ cm^{-1}$; after chemical polish, $\alpha = 0.014\ cm^{-1}$.

(e) Boule cut with string saw, followed by mechanical lap and polish.

TABLE II

INVENTORY OF SAMPLES FOR TRANSMISSION ELECTRON MICROSCOPY

Sample No.	Optical Absorptivity at 10.6μm (cm^{-1})	Foil Orientation	Preparation Method[a]
Completed			
1857T	0.013	(111)	I
		(111)	II
1860T	0.018	(111)	I
		(111)	II
1852T	0.031	(111)	I
Scheduled			
1852T	0.031	(110)	III
1857T	0.013	(111)	IV
		(110)	III
2602-10	0.016	(111)	III

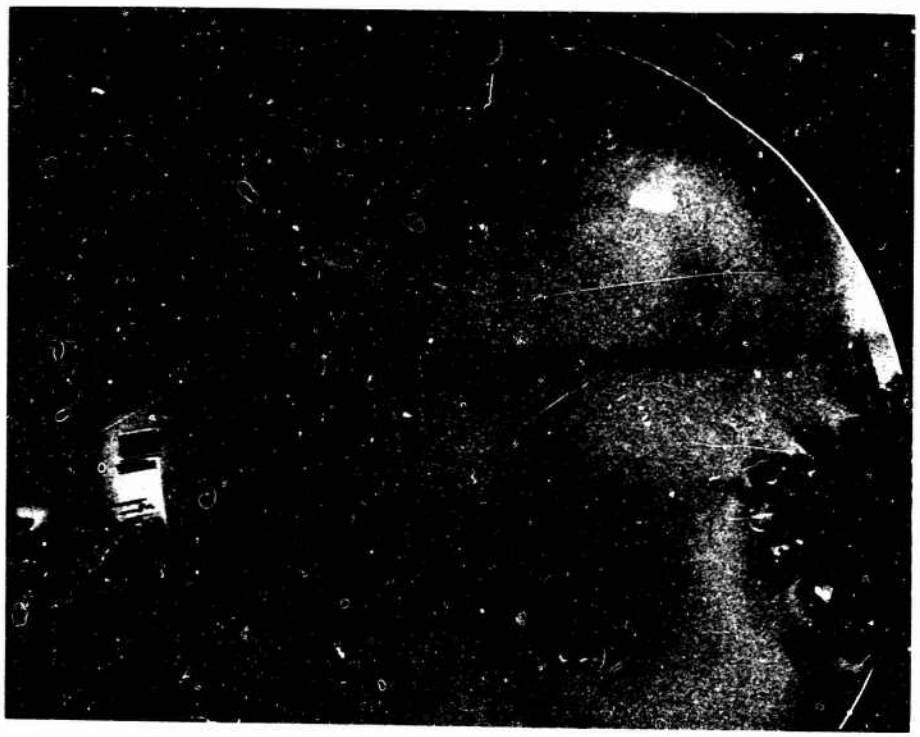
(a) Foils were prepared by the following methods:

I - Ion thinned to ∿3μm; ion thinned for TEM

II - Ion thinned to ∿3μm; chemically thinned for TEM

III - Mechanically thinned to ∿3μm; ion thinned for TEM

IV - Mechanically thinned to ∿3μm; chemically thinned for TEM

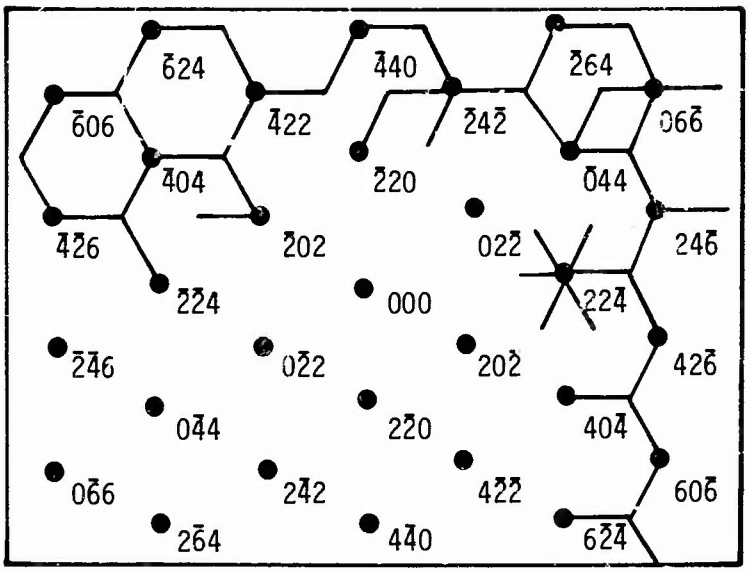


(a) 3.5X

(b) 30X

FIGURE 1 BACK REFLECTION X-RAY TOPOGRAPHY OF GaAs SAMPLE NO. 6005B, (422) REFLECTION, CuKα RADIATION: (a) EDGE DEFECTS CAUSED BY LOSS OF B_2O_3 ENCAPSULANT, (b) SURFACE DAMAGE RESULTING FROM MECHANICAL POLISHING

FIGURE 2 TRANSMISSION ELECTRON MICROGRAPH AND CORRESPONDING DIFFRACTION PATTERN SAMPLE 1857T, DARK FIELD, (220) REFLECTION, 120 KV BEAM (212,000X)



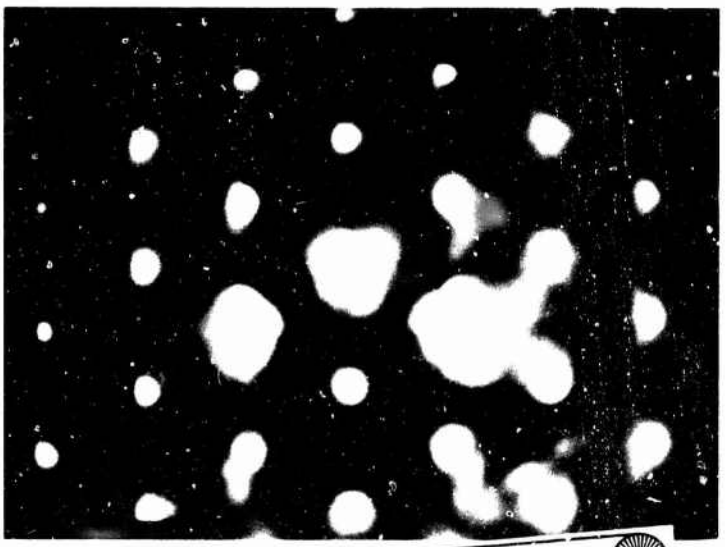


FIGURE 3 ELECTRON DIFFRACTION PATTERNS OF (111) ORIENTED FOIL, SAMPLE 1857T, 120 KV BEAM

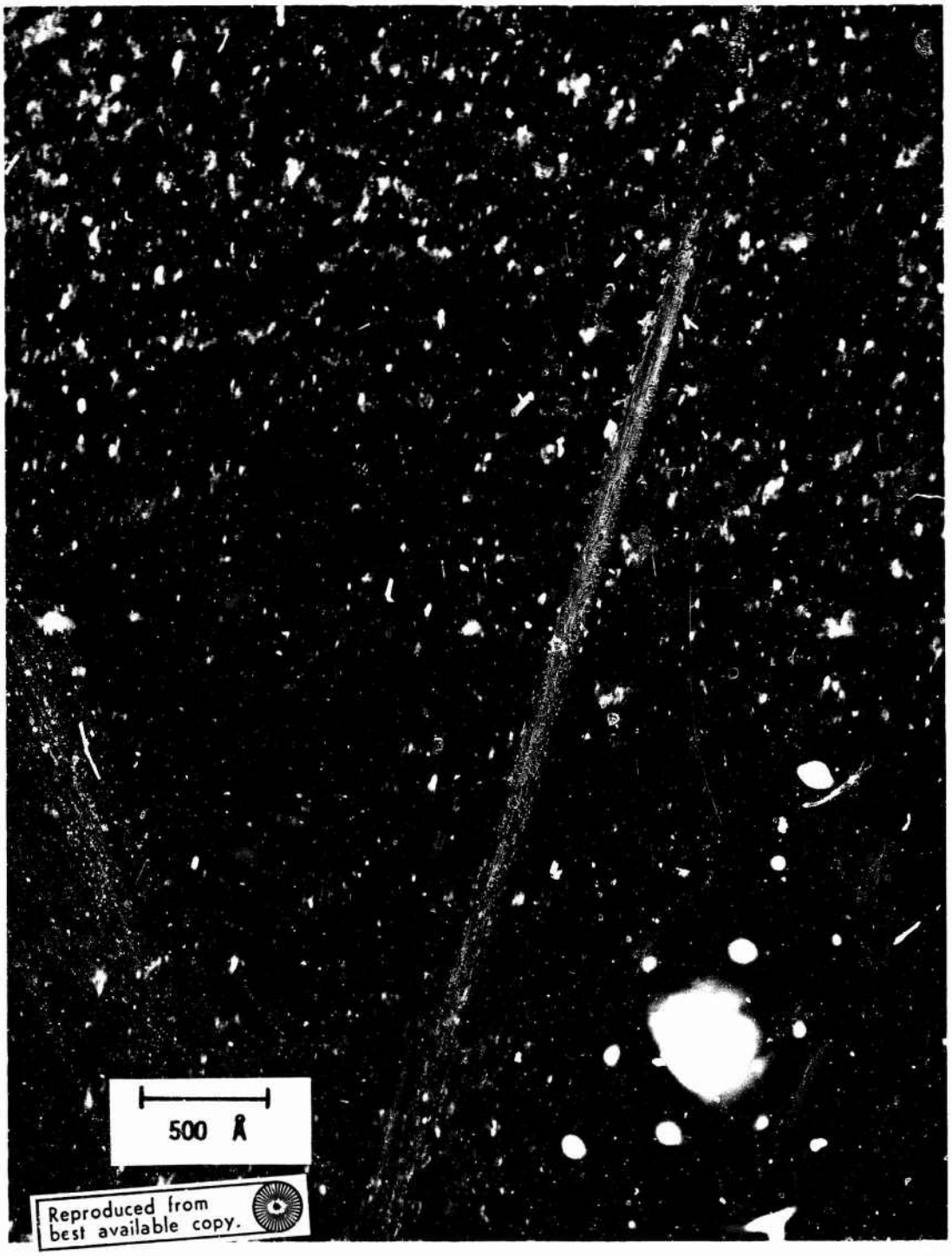


FIGURE 4 TRANSMISSION ELECTRON MICROGRAPH AND CORRESPONDING DIFFRACTION PATTERN OF SAMPLE 1852T, WEAK BEAM, 120 KV BEAM (408,000X)

CAMBRIDGE,
MASSACHUSETTS

CHICAGO
NEW YORK
SAN FRANCISCO
WASHINGTON
ATHENS
BRUSSELS
CARACAS
LONDON
MEXICO CITY
PARIS
RIO DE JANEIRO
TORONTO
ZURICH